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ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

September 12, 1966

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Panama City, Florida 32401

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Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 1, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for August 1966

Gentlemen:

Work was initiated in July and expanded in August.

The development of a theory for bubbles rising freely in a liquid is aimed toward predicting the size, rate of rise, and gas content of the bubble which can be compared with experimental data.

Liebermann<sup>1</sup> gives what appears to be adequate treatment of a stationary bubble containing a single gas when the water (distilled) contains the same gas. However, figure 2, page 207, showing the final results compared with experiment, contains plotting errors. A request has been sent to Dr. Liebermann for the original data.

Blanchard and Woodcock<sup>2</sup> following Wyman et al.<sup>3</sup> discuss the free bubble by assuming that the diffusion takes place through a thin uniform shell. This is a good first step toward solving the general problem.

Levich<sup>4</sup> considers diffusion and hydrodynamic problems of a quite general nature and will be the main reference for future work.

The general problem may be stated as follows: A bubble having initial radius  $R$  containing a single gas (besides water vapor) is

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released at a depth  $h$  in sea water. What is the radius  $R$  of the bubble, rate of rise  $u$  of the bubble, and concentrations of various gases in the bubble as a function of time? Dissolved gases in the water diffuse into the bubble; the initial gas diffuses out.

A mathematical formulation of the problem which includes all observed phenomena is in progress. A close study of available experimental results is continuing. Various aspects are not yet clear, in particular with regard to the effect of surface-active agents.

The equation governing the diffusion of gases is

$$D \nabla^2 c - \vec{v} \cdot \nabla c - \frac{\partial c}{\partial t} = 0$$

where  $c$  is the concentration of the gas,  $D$  the diffusion constant and  $\vec{v}$  the flow velocity of the water. Determination of  $\vec{v}$  is largely a hydrodynamics problem, complicated by the presence of surface-active agents. Levich deals with some aspects of this problem. Surface-active agents affect the boundary condition at the bubble surface for both the hydrodynamics equations and the diffusion equation. The effect of boundary conditions on the hydrodynamics is significant as shown by the work of Rybezyński and Hadamard.<sup>5</sup>

Just how surface-active substances affect the boundary conditions for the diffusion equation is not understood. Liebermann indicates that the rate of diffusion is noticeably changed by the presence of surface contaminants, although the rate of diffusion is not changed by more than a factor of two. Surface-active agents decrease the surface tension, hence decrease the pressure inside the bubble and the rate of diffusion.

The effect of changing depth appears to be reasonably straight-

forward. Behavior with varying temperature is somewhat complicated and will be neglected in the initial formulation.

At present the mathematical details are being studied closely. Several physical approximations which will greatly simplify the problem will probably be possible. Necessary mathematical techniques and approximations will require careful investigation.

### Experimental Program

The immediate objective of the experimental program is to perfect means of making accurate bubble size determinations for hydrogen bubbles in sea water. The method employed is a modification of that used by Blanchard and Woodcock (2). The bubbles are generated in a tank 10 inches in height filled with water. The upper surface of the tank is glass, except for a 2 in. x 3 in. cut-out, which is covered with 1-mil Mylar film, drawn taut, and cemented in place. The under surface of the Mylar is rendered hydrophobic by the application of a suitable silicone oil; bubbles impinging against this surface establish a zero contact angle and, consequently, are not seriously distorted.

A photographic plate or film is laid onto the upper surface of the Mylar film, emulsion side against the film. Flash illumination from below is made with suitable collimated light, or alternately, by point-source light from such distance that the bubble diameter is negligible by comparison. The developed plate is examined under suitable magnification, and measurements of bubble diameter are made by optical micrometry.

Initial measurements will be made on bubbles generated from cylinder gas at a suitable orifice. Later experiments will utilize chemical sources dispersed in the water. Studies will include gas exchange with sea water.

Respectfully submitted

Arthur L. Bennett  
Project Director

ALB/st

REFERENCES

1. L. Liebermann, "Air Bubbles in Water," J. Appl. Phys. 28, 205-211 (1957).
2. D. C. Blanchard and A. H. Woodcock, "Bubble Formation and Modification in the Sea and its Meteorological Significance," Tellus, 9, 145-158 (1957).
3. J. Wyman, Jr., P. I. Scholander, G. A. Edwards, and L. Irving, "On the Stability of Gas Bubbles in Sea Water," J. Marine Res., 11, 47-62 (1952).
4. V. G. Levich, Physicochemical Hydrodynamics, (Transl. Scripta-Technica, Inc.) Prentice-Hall (1962).
5. See, e.g., B. T. Chao, Motion of Spherical Gas Bubbles in a Viscous Liquid at Large Reynolds Numbers, Physics of Fluids, 5, 69-79 (1962).

## GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA 30332

6 October 1966

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Commanding Officer and Director  
U. S. Navy Mine Defense Laboratory  
Panama City, Florida 32401

Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 2, Project A-956, Bubble  
Screen Dynamics, Contract Nonr-991(14), for  
September, 1966

Gentlemen:

The theoretical work has clarified the mathematical statement of mass transfer pertaining to the rising bubble. Physical approximations are being examined for compatibility with mathematical techniques in preparation for computation.

Dr. Liebermann (U. of Cal., San Diego) confirmed the validity of his experimental measurements. The data do conform to the expected theoretical trend. The location of the straight dashed line in Fig. 2 is misleading.

Early experimental work with a Mylar film window on the top of the 10-inch tank indicated that the gas bubbles wetted the film preferentially. Instead of a contact angle (measured through the liquid) of  $0^\circ$  as desired, the angle approached  $180^\circ$ . The bubbles on the film were shallow caps of a sphere instead of the nearly spherical shape desired for measurement.

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Search for a film of suitable surface characteristics combined with the needed mechanical properties was not too successful. The desired result appears to be obtained by immersing the 2-inch-square lantern-slide plates in the water. The bubbles are collected on the emulsion facing down. A bare Strobotron bulb oriented so that the spark discharge in argon is nearly end-on to the plate at a distance of about 15 inches serves as a point source. Two flashes at 1/4 second interval of the stroboslave at high intensity provide good images.

Possible solid and liquid carriers for finely divided lithium hydride have been studied. The desired properties are a density comparable to that of the active solid to maintain a uniform distribution, chemical stability, and rapid solution in water. At present experiments are being done with ketones, which appear promising.

Equipment is being designed for introduction of the slurry into a stream of water, dispersion of the bubbles, and sampling with the coulter counter to facilitate statistical measurements of bubble size.

Respectfully submitted,

Arthur L. Bennett  
Res. Prof. of Physics

ALB/srt



ENGINEERING EXPERIMENT STATION  
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Physical Sciences Division

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3 November 1966

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Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 3, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for October, 1966

Gentlemen:

Work is continuing on the general theory of diffusion of gas from a rising bubble. Work has begun on the analysis of mass transfer on the Stokes circulation hypothesis, pertinent to hard spheres. This approximation is applicable to air bubbles of diameter up to 150 microns in water, according to Garner and Hammerton.<sup>1</sup> These workers found the transition from no circulation (Stokes) to full circulation with much higher mass transfer covered the range from 150 microns to 2500 microns. Since we are interested in the lower part of the transition range, the first approximation noted above will be checked against other measurements.

The suspension of lithium hydride in Methyl ethyl ketone is improved by the addition of Union Carbide Tergitol surfactant NPX. This combination looks promising for a liquid carrier. A ketone of higher density, 2-4- pentane dione has been ordered to permit a closer adjustment of the density of the carrier liquid.

The behavior of the slurry on introduction to the water tank is encouraging. The equipment for mixing a small stream of the slurry into a water stream is progressing, in preparation for bubble measurements.

Respectfully submitted,

Arthur L. Bennett  
Project Director

ALB:srt

REFERENCE:

1. F. H. Garner and D. Hammerton, "Circulation Inside Gas Bubbles," Chem. Eng. Science, v.3, 1-11, 1954.

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U. S. Navy Mine Defense Laboratory  
Panama City, Florida 32401

PATENT 2-10 1967 BY JH  
FORMAT 2-10 1967 BY JH

Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 5, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for December 1966

Gentlemen:

Several attempts were made to disperse lithium hydride in DMSO with various gelling agents, e.g., Carbopol 943, Bentone 34, Bentone 38, Cabosil M-5. All these attempts produced a more or less satisfactory gel, but when a material was injected into water through a small-bore hypodermic needle it produced strings of the injected material. The resulting drops did not react within the flow tube in the 10-second transit time although dispersion occurred later in the system. Even the addition of 1% of Tergitol XC did not result in satisfactory behavior.

Tetrahydrofuran was then tried as a carrier. The density, 0.89, is about 10% higher than the nominal density of LiH. About two thirds of the solid, however, floated on the liquid, nearly a third sank, but an appreciable quantity remained in suspension. Micromerograph runs of a dried sample of each indicates that the floating component has a somewhat larger particle size; the other two components are close to the original size distribution.

A portion of the middle fraction in tetrahydrofuran was titrated with water. The LiH content was 1.5 mg/ml. This suspension was injected through a No. 26 needle (0.010 inch I.D.) with repeated good results over 5 separate runs with the Coulter Counter. After about 1 hour, however, repeated stoppage occurred in the needle, due to clumping together of the small crystals into aggregates. These aggregates were broken up by 30 seconds of ultrasonic agitation.

Previous Coulter Counter runs have been impaired by the rapid settling of the solid in the syringe used for injection. This difficulty has been reduced

by placing two 1/10-inch stainless steel balls in the syringe. An air driven magnetic actuator close to the barrel of the syringe then gives vigorous stirring of the dispersion.

Coulter Counter runs with the LiH suspended in tetrahydrofuran with the stirrer in use have been analyzed. The injection rates used were  $6.5 \times 10^{-8}$  and  $1.1 \times 10^{-7}$  gm of solid/ml of 1% NaCl solution. The expected bubble size distribution was computed from the Micromerograph measurement of particle size distribution. The bubble counts at 50 microns diameter are about 40% of the predicted number. The bubble count is progressively lower for larger bubbles to less than 10% at 200 microns. The discrepancy is believed to be due to two causes:

a) The Micromerograph gives too high a count of the large particles due to agglomeration as a result of the nitrogen blast which disperses the material in the gas column for measurement of rate of fall vs time;

b) The handling of the suspension, despite care in dispersing the solid before transfer and during injection, permits loss of the larger particles.

In addition to the finely divided LiH (2 to 25  $\mu$ , Micromerograph) which has been in use, a coarser crushed powder (4 to 100  $\mu$ ), spherical LiH particles, and a dispersion of Li metal in mineral oil are now available.

Respectfully submitted,

Arthur L. Bennett  
Project Director

ALB:srt



ENGINEERING EXPERIMENT STATION  
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Physical Sciences Division

13 February 1967

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~~13~~ 9-27-67  
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Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 6, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for January 1967

Gentlemen:

The lithium metal in mineral oil from Lithium Corporation of America has been examined under the microscope. The particles generally approach a spherical shape. The median size of a limited sample count is about 16 microns with a measured range of 3 to 55 microns. The low density of the metal, 0.534 at 20°C, is difficult to match in a liquid. Several hydrocarbons in the density range 0.605 to 0.59 have been tried. The stability of the suspension is promising, but the insolubility of the carrier liquid prevents bubble formation when the suspension is injected into water. Inert drops of carrier form during slow injection of a dilute suspension into water. Search for a more suitable liquid and a thickener is continuing.

Our experience with a liquid suspension combined with the required complexity of a dispenser indicates that a finely divided solid diluent may be more promising. The approach contemplated is to increase the density of a pellet by diluting the active agent with a dense powder to achieve a high sinking rate for a bare pellet. As the pellet falls, the reaction at the surface will dislodge each bubble as it is generated. A suitable binder will permit the inert material to disperse so that the active surface is continually renewed.

Pellets about 1/4 inch in diameter were formed with the following composition:

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13 February 1967

15 wt% Lithium Metal 46.3% in oil  
79 wt% Lead Powder (Glidden Co. Grade F)  
8 wt% Tergitol XC Dispersant

These pellets when dropped in a glass jar two feet high fell at a rate of about one foot a second. The reaction was vigorous and created a column of bubbles which dispersed laterally as the individual bubbles rose. There appeared to be negligible coalescence of bubbles while the pellet was falling. When the pellet reached the bottom, however, bubbles of millimeter diameter predominated.

Lithium hydride in the following composition was tried:

10 wt% Lithium Hydride  
80 wt% Lead Powder, Glidden Co. Grade F  
10 wt% Tergitol XC Dispersant

The behavior was inferior to the metal composition; reaction occurred at the surface without disintegration of the inert carrier. Gas bubbles gathered on the surface and grew to a size depending on the pellet velocity.

A transparent tank 6-inches O.D., six feet high is being assembled for continuation of the tests.

Respectfully submitted,

Arthur L. Bennett  
Project Director

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10 March 1967

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Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 7, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for February 1967

Gentlemen:

A sample of Baker Castor Oil Co. thixotropic agent MPA-60 has been received. The material is believed to be a polyolefin wax in xylene. There appears to be no reaction with Li even at 200° F. Our earlier suspicion that Li metal reacts with ketones appears to be confirmed by current experiments. The search will continue for a suitable liquid suspension.

Experiments with a mixture of solids continues. The 6-inch O.D. lucite tank 6 feet tall has been put to use. High speed movies of a number of solid pellets were taken with a Mitchell 16-mm camera with Tri X film at 128 frames a second as summarized in Table I.

A copy of the film will be edited for forwarding to the MDL.

Preparation of a Final Technical Report has begun.

Respectfully submitted,

Arthur L. Bennett  
Project Director

ALB:srt

<u>Serial No.</u>	<u>Lens</u>	<u>Dist.</u>	<u>Pellet Formula</u> *	<u>Tergitol Surfactant</u>	<u>Lighting</u> **
A-1 & 2	25 mm	5 ft.	Li-1	NPX	Back
3 & 4			Li-2	XC	
5 & 6			LiH-1	XC	
B-1	50 mm	4 ft.	Li-1	NPX	
2			Li-2	XC	
3			LiH-1	XC	
C-1	50 mm	4 ft.	Li-1	NPX	Side
D-1			Li-1	NPX	Back
2	100 mm	4 ft.	Li-2	XC	
3			LiH-1	XC	

\* Formulation

Li-1	14.15%	Lithium Metal 46.3% in oil
	85.1 %	Lead Powder Glidden Co. Grade F
	0.75%	Tergitol NPX Dispersant
Li-2	15.4%	Lithium Metal 46.3% in oil
	77.0%	Lead Powder Glidden Co. Grade F
	7.6%	Tergitol XC Dispersant
LiH-1	10%	Lithium Hydride Powder
	80%	Lead Powder Glidden Co. Grade F
	10%	Tergitol XC Dispersant

\*\* Back lighting: two 1000-w photofloods beside tank at 135° to camera axis toward diffusing back drop. Side lighting: one 1000-w photoflood 2 1/2 ft. left of tank perpendicular to camera axis.



ENGINEERING EXPERIMENT STATION  
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5 April 1967

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Panama City, Florida 32401

Attention: Dr. E. A. Hogge, Code 710

Subject: Letter Report No. 8, Project A-956, Bubble Screen  
Dynamics, Contract Nonr-991(14), for March 1967

Gentlemen:

The Baker Castor Oil Co. MPA-60 has not provided a stable suspension. This material has been tried as a 1% addition to DMSO, tetrahydrofuran, dimethylbutane, and xylene. A thixotropic effect was obtained only with xylene; with lithium metal added, non-reacting strings were produced on injection into the tank. The addition of 1% NPX made no substantial improvement. MPA is not compatible with the few liquids known to be non-reactive with lithium but readily soluble in water.

At this stage the solid dispersion of the reactive powder is much more promising as material which will retain its characteristics over a long period of time. A liquid suspension, however, would be valuable for laboratory experiments because of the ease of introducing a controlled amount of material.

A solid suspension appears to be most promising. Further experiments should soon lead to a mixture with the desired characteristics of controlled release rate and bubble size distribution. The available funds, however, have been exhausted and further experimental work is not possible at this time.

Work on the technical report is going forward.

Respectfully submitted,

Arthur L. Bennett  
Project Director

ALB/srt

FINAL REPORT

PROJECT A-956

BUBBLE SCREEN DYNAMICS



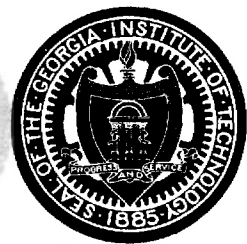
Arthur L. Bennett

Contract No. NONR-991 (14)

May 1969

Prepared for

Naval Ship Research and Development Laboratory  
Panama City, Florida



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Engineering Experiment Station  
Atlanta, Georgia

FINAL REPORT

PROJECT A-956

BUBBLE SCREEN DYNAMICS

By

ARTHUR L. BENNETT

Contract No. NONR-991 (14)

May 1969

Prepared For  
NAVAL SHIP RESEARCH AND DEVELOPMENT LABORATORY  
PANAMA CITY, FLORIDA

## I. INTRODUCTION

The objective of this study is to develop the research background required for the development of bubble generating devices for the deployment and maintenance of bubble screen for specific applications requiring a decrease in the acoustic transmission in a given direction for a specific band of frequencies.

The acoustic transmission is most strongly influenced at the resonant frequency of bubbles in the acoustic path. The objective, therefore, is to produce a distribution of bubble sizes which will provide the required number of bubbles of each size to cause the desired attenuation at the place required. Since the bubble size is time-dependent due to gravity and diffusion effects, the duration of the effectiveness of a screen requires the prediction of bubble dynamics, i.e., the variation in time of the size and location of each individual bubble. With this prediction the extent and duration of the effectiveness of the curtain can be computed.

This study pertains to the control of the bubble size distribution by the generation of individual bubbles by chemical action. A water-reactive chemical is to be used which will produce an independent bubble of a size controlled by the particle size of the active chemical. The particles will be introduced in the volume to be treated in the number, size, and space distribution required to produce the desired acoustic effect. The scope of the current work is limited to the theoretical and experimental techniques required for the creation of the bubbles and the analysis of bubble dynamics as defined above.

## II. DYNAMICS OF AN INDIVIDUAL BUBBLE

Velocity of Rise. A given volume of gas released at a known depth

in water will produce a sphere because of surface tension at the interface. Since the density of the gas is usually negligible relative to that of the water, the buoyant force causes the bubble to rise. After the initial acceleration a steady rate of rise is attained when the buoyancy is balanced by the drag. Bubbles with radii greater than about 0.04 cm will be distorted by the pressure variation over the bubble surface due to the flow distribution.

The rate of rise is strongly dependent on the size of the bubble and on the presence or lack of motion of the bubble surface (circulation). For the smallest bubbles (Reynolds No.,  $Re < 1$ ;  $r < 0.005$  cm) there is little doubt that bubbles behave like solid spheres, hence follow Stokes Law:

$$U = - 2(\rho_1 - \rho_2) g r^2 / 9\mu ,$$

where  $U$  is the velocity (upward as indicated by the sign),  $\rho_1$  is the density of the liquid,  $\rho_2$  the density of the gas (usually negligible so  $\rho_1 - \rho_2$  may be replaced by  $\rho_1$  of the liquid),  $g$  is the gravity acceleration,  $r$  the radius of the bubble, and  $\mu$  the absolute viscosity of the liquid.

A study of the behavior of fluid drops moving in a liquid was carried out independently by J. Hadamard and W. Rybcyński in 1911. The development of the theory is followed in detail by Levich.<sup>1</sup> This theory applies only where the circulation of the liquid over the surface is fully developed. In this case the velocity is  $3/2$  the Stokes velocity. Experimental data indicate that this theory does not apply to gas bubbles in water, as indicated below.

A careful study of bubbles in a variety of fluids was carried out by Garner and Hammerton.<sup>2</sup> They observed the internal circulation of bubbles by introducing an ammonium chloride fog during the formation. They find that bubbles rise like rigid spheres for radii below 0.05 cm ( $Re < 100$ ). For diameters of 0.1 to 0.15 cm the path becomes helical with a pitch and diameter of about two bubble diameters. The bubble is flattened; a long axis of the ellipsoidal shape follows the helix. At a radius of about 0.25 cm the helical motion is interrupted by periods of straight vertical rise. Bubbles above 0.4 cm radius have a helispherical cap and a flattened posterior. Measurements by Garner and Hammerton<sup>2</sup> of bubble velocity vs. diameter and by Coppock and Meiklejohn<sup>3</sup> are similar to the more detailed measurements next described.

Haberman and Morton<sup>4</sup> at DTMB carried out extensive bubble measurements in many liquids in tanks large enough to be nearly free of wall effect. The conventional drag coefficient  $C_D$  for a bubble rising at terminal velocity  $U$  in terms of the equivalent radius of a sphere of the same volume as the bubble may be written:

$$C_D = \frac{8gr}{3U^2} ,$$

where  $g$  = gravity acceleration,  
 $U$  = velocity of rise,  
 $r$  = equivalent radius.

The  $C_D$  of small bubbles follows Stokes Law for  $Re < 1$ .

At larger  $Re$ , tap water at 21° follows the  $C_D$  of rigid spheres (Goldstein<sup>5</sup>) to a  $Re$  of about 40. At still larger  $Re$ ,  $C_D$  of tap water is

slightly less than that of spheres to the minimum  $C_D$  of 0.6 at  $Re = 400$  where the curves cross.  $C_D$  for tap water then rises to 2.5 at  $Re \approx 4000$ , approximately where spherical-cap bubbles form, and remains constant at higher  $Re$ .

Filtered water shows substantially lower  $C_D$  from  $Re$  about 50 to a minimum of 0.16 at  $Re$  about 450; the  $C_D$  then rises to join tap water at  $Re > 1200$ . Water with 0.42% by volume of GLIM (a surface-active detergent) with a solution surface tension of 33 dynes/cm shows higher  $C_D$  than solid spheres and tap water from  $Re$  about 200 to about 2000. The rise velocity  $U$  in terms of equivalent radius is given in Figure 1. The curve for tap water at  $21^\circ C$  is of prime interest since it is believed to be representative of what should be expected in sea water at this temperature. The deviation of this curve from the curve for filtered water at  $19^\circ C$  (Rosenberg<sup>6</sup>) shows the effect of the contaminants normally present in tap water. Haberman and Morton provide good data on filtered water at  $6^\circ C$  indicating the effect of the viscosity of water up to a radius of 0.08 cm. The temperature effect apparently is negligible for ellipsoidal and larger bubbles in pure water. For small bubbles ( $< 0.01$  cm) Stokes Law indicates that the velocity should vary inversely with the viscosity, i.e. the velocity should double from  $5^\circ C$  to  $30^\circ C$ .

The maximum effect of a surface-active agent is shown by the drop in velocity from 34 cm/sec for a bubble of radius 0.07 cm in distilled water at  $19^\circ C$  to 15 cm/sec in the presence of 0.45% GLIM. Stuke<sup>7</sup> investigates the effect of caproic acid on hydrogen bubbles in pure water at  $19^\circ C$ . The effect of a  $1.5 \times 10^{-4}$  molar solution (concentration  $2 \times 10^{-5}$ ) at this diameter was about half the effect of stronger solutions of  $4.5 \cdot 10^{-4}$  molar and  $2 \cdot 10^{-2}$  molar. It is evident that a minute contamination of

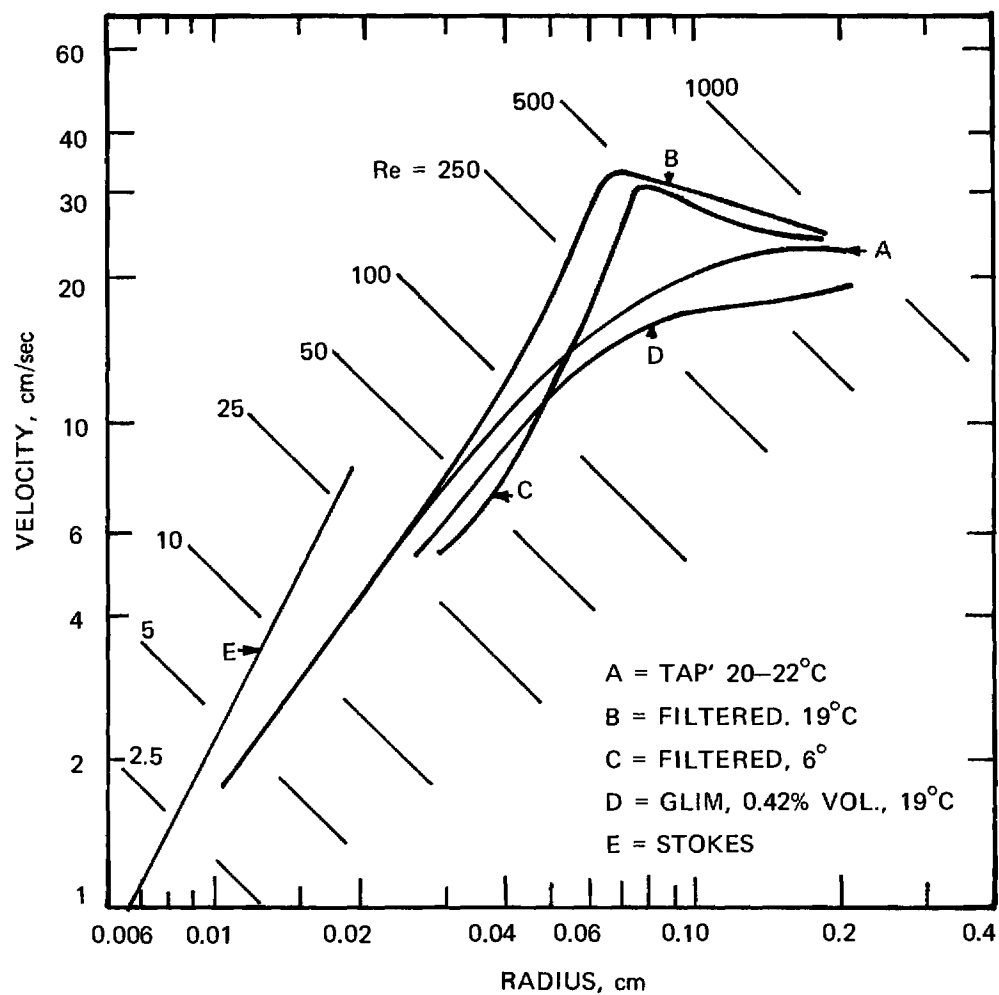


Figure 1. Velocity of rise of bubbles in water.  
Reynolds No.,  $Re$ , for 20°C.

surfactant has a significant effect.

Turner<sup>8</sup> found a significant change in bubble behavior depending on whether the tap water came from a clean river or one polluted with detergents in concentration less than  $10^{-6}$ . MacIntyre<sup>9</sup> noted that bubbles in water double-distilled and condensed in a silica tube would rise 15 cm with low drag corresponding to circulation and then would be checked abruptly as the drag increased, presumably because the bubble surface had picked up either particulate matter not removed in the purification or airborne surfactant. Levich<sup>10</sup> believes that contamination by surfactants is almost universal. The conclusion is that water exposed to the air accumulates enough material, whether organic surfactant or finely divided solid, to stop the internal circulation. Therefore, for waters of interest in this study, one should use the measured drag of solid spheres to represent the behavior of bubbles from the smallest (Stokes Law) to the formation of ellipsoidal bubbles at  $Re \sim 250$ , corresponding to a radius of about 0.08 cm in tap water at  $21^{\circ}C$ .

In sea water, the effect of organic material would be expected to slow the rate of rise further, as indicated in Fig. 1 for GLIM, over the range of radii from 0.02 to 0.5 cm. Measurement of the effect of the abundant particulate matter in sea water is not available. In a preliminary examination of the flow streamlines about a spheres of the range of size of particular interest, MacIntyre<sup>9</sup> found that the streamlines approach the surface closely.

## II. GAS TRANSPORT

Bird, Stewart and Lightfoot<sup>11</sup> give a broad treatment of transport phenomena. The diffusion transfer of gas across the bubble surface de-

depends on the concentration of the dissolved gases in the liquid, the total pressure in the bubble, the concentration of each gas both in the bubble and in the liquid, the multicomponent diffusion coefficients of the gases present, and the rate of renewal of the liquid in contact with the bubble surface. We shall consider here a bubble of hydrogen in sea water in an isothermal system.

Gas transport through the bubble surface is controlled by a thin layer of liquid since diffusion in the liquid is slow compared to that in gas. The transport rate therefore is strongly dependent on the hydrodynamic flow profile of this surface layer.

As was indicated above, the drag measurements indicate that in natural water, and particularly in sea water, surface contamination will not permit circulation of the bubble surface for long. Levich considers bubble rise and gas transfer at length, but mistakes must be corrected.<sup>12</sup>

Two papers pertinent to the gas transfer from rising bubbles appeared nearly simultaneously, by Ruckenstein,<sup>13</sup> and Lochiel and Calderbank.<sup>14</sup> The latter author's discussion of particular solutions pertaining to the immobile surfaces of spheres are summarized.

In creeping flow (Stokes), they obtain the Sherwood number,  $Sh$ ,

$$Sh = 0.99 Pe^{1/3} \quad \text{for } Re < 1, Pe > 10^2,$$

where  $Re$  is the Reynolds No. and  $Pe$  the Peclet No. (see below for definitions). For  $Re \gg 1$ , the Navier-Stokes and continuity equations, in forms applicable to boundary layer flow are integrated to give the Karman Integral Relation for three-dimensional axisymmetric flow. For a solution



a velocity profile in the boundary layer is needed; the authors use the quartic profile of Pohlhausen with the boundary conditions at the gas surface and at the external surface of the boundary layer.

The result is the Sherwood number as a function of the angle  $\theta$  from the apex of the advancing spherical bubble. At the high Re considered, flow separation occurs at  $\theta = 108^\circ$ . On the assumption that the above equation holds for  $0^\circ \leq \theta \leq 108^\circ$  and that the transfer in the wake region is 20% of the frontal transfer (according to Frossling) the result is

$$Sh = 0.84 Re^{1/2} Sc^{1/3}$$

or

$$K_L = 0.84 D^{2/3} d_e^{-1/2} (\rho_c/\mu_c)^{1/6} U^{1/2}$$

where

$$Sh = \text{Sherwood No.} = k_L d_e D^{-1}$$

$$Re = \text{Reynolds No. in external fluid} = d_e U \rho_c \mu_c^{-1}$$

$$Pe = \text{Peclet No.} = d_e U D^{-1}$$

$$Sc = \text{continuous phase Schmidt No.} = \mu_c \rho_c^{-1} D^{-1}$$

= ratio of the thickness of the hydrodynamic boundary layer to the diffusion boundary layer.

and

$k_L$  = continuous phase mass transfer coefficient,  $\text{cm}^2 \text{sec}^{-1}$

$d_e$  = equivalent spherical diameter, cm

$D$  = diffusion coefficient of solute in solvent (external fluid),  $\text{cm}^2 \text{sec}^{-1}$

$U$  = velocity of translation,  $\text{cm sec}^{-1}$

$$\begin{aligned}\mu_c &= \text{coefficient of viscosity in the external fluid, gm sec}^{-1} \text{ cm}^{-1} \\ \rho_c &= \text{density of external fluid, gm cm}^{-3}\end{aligned}$$

The value of the constant 0.84 on the above assumptions lies in the range of the experimentally measured values for solid spheres, 0.42 and 0.95. The value at the front stagnation point of 1.34 is in reasonable agreement with Froessling's 1.47 from rigorous analysis.

From the Sherwood No. thus derived, the mass transfer coefficient  $k_L$  is obtained. The transfer rate,  $N$  ( $\text{cm}^3 \text{sec}^{-1}$ ), from Fick's Law, is

$$N = k_L A (C_* - C_o) ,$$

where  $A$  is the surface area,  
 $C_*$  is the concentration at saturation,  
 $C_o$  is the concentration in the undisturbed fluid.

and therefore the rate of change of diameter can be derived.

This analysis does not include the effect of increased internal pressure in the bubble due to surface tension. Over the range of bubble radii of interest, 0.03 cm to 0.003 cm, the overpressure in a bubble in pure water due to surface tension ( $= 2\gamma/r$ ) will range from 0.0046 At to 0.046 At. The depth considered is from the surface (1 At) to perhaps 20 meters (3 At total).

The two cases summarized above do not apply to most of the range in bubble radii of interest corresponding to the gap in Reynolds numbers from 1 to about 40 (covering the radii from 0.01 to at least 0.03 cm, resonance

frequency from about 30 to 10 kHz). MacIntyre<sup>15</sup> used a new approach in an attempt to fill the gap. The computer program was not carried to a useful stage for this analysis. His figure 6.3 does, however, shed light on the behavior of a streamline very close to the stationary bubble surface, within the region of molecular diffusion, for  $5 \leq Re \leq 40$ .

Solubility of Gases. As noted above the mass transfer coefficient depends on the saturation concentration or solubility. The partial pressure of nitrogen is usually in equilibrium with the nitrogen in the air, that is, the water is saturated at the water temperature and nitrogen partial pressure at the surface. Mixing appears to be adequate to maintain the same amount of dissolved gas at depth.<sup>16</sup> The degree of saturation therefore decreases with depth, following Henry's Law.

The oxygen concentration varies with biological consumption and production. The oxygen concentration varies widely with geographical location, season, and time of day.

The solubility ratios of nitrogen, oxygen, and argon were carefully measured by Benson and Parker.<sup>17</sup> The solubilities and ratios of previous measurements were discussed and acceptable values stated both for distilled water and for sea water.

The solubility of gases in sea water is reduced relative to distilled water by dissolved salts -- the "salting-out" effect. Green and Carritt<sup>18</sup> measured the solubility of oxygen in sea-water at 22°C as a function of chlorinity; their data indicate a solubility relative to distilled water of about 0.81 at 19.5/1000 chlorinity. The dependence on temperature is relatively small; about 0.78 at 0°C to 0.82 at 25°C. These values are consistent with the solubility coefficients and solubilities for nitrogen given by Benson and Parker.<sup>17</sup>

The solubility ratios and the solubilities  $O_2'$  and  $N_2'$  (cc gas/l in equilibrium with dry atmosphere at 760 mm Hg) considered best<sup>17</sup> for sea-water of chlorinity 20/1000 follow:

Temp°C	0	5	10	15	20	25	30
$N_2' / A'$	37.48	37.74	38.00	38.26	38.52	38.78	39.05
$N_2' / O_2'$	1.807	1.827	1.847	1.866	1.886	1.906	1.926
$O_2'$	7.97	7.07	6.36	5.78	5.31	4.89	4.46
$N_2'$	14.30	12.73	11.56	10.57	9.77	9.10	(8.57)

The volume solubility coefficient (cc/liter of dry gas at 760 mm) of hydrogen is comparable to nitrogen over the temperature range of interest (Handbook). The salting-out effect is less than that of oxygen.<sup>19</sup> The resulting solubility in sea water is poorly established. Since one can expect negligible hydrogen in solution in sea water, outward diffusion can be expected to be strong but partially compensated by inward diffusion of nitrogen and oxygen.

Diffusion. In the analysis of gas transport above, it is seen that the mass transfer depends on the diffusion coefficient of the gas in the liquid. The available data generally apply only to the diffusion of a single gas. Lightfoot and Cussler<sup>20</sup> have recently summarized the status of methods of prediction of diffusion coefficients, including binary systems. They note that no method is available for prediction in multi-component systems.

Data on diffusion coefficients for dissolved gases are provided by Houghton, et al.<sup>21</sup> who measured the rate of dissolution in small station-

ary bubbles of a number of gases, including hydrogen, oxygen, and nitrogen in water, sea water, and water with surfactants. They found no significant difference, within the measured internal average deviation of 10%, in the coefficient for air in pure water and in sea water. The values derived depends on the solubility of the gases which are not reliably known. The diffusion coefficients measured were compared with earlier data.

Wise and Houghton<sup>22</sup> applied the same technique to an extended list of gases over the temperature range of 10° to 60°C and compared the results with theory. The binary diffusion coefficients,  $D_L$ , for the gases of interest are tabulated with the solubilities,  $\alpha$ , used:

System	Temp (°C)	$\alpha(\text{ccNTP/cc})$	$D_L \times 10^5 \text{ (cm}^2\text{/sec)}$
$\text{H}_2/\text{H}_2\text{O}$	10	0.0189	4.6
	20	0.0174	5.0
	30	0.0163	7.0
$\text{O}_2/\text{H}_2\text{O}$	10	0.0410	1.7
	20	0.0323	2.3
	30	0.0271	2.8
$\text{N}_2/\text{H}_2\text{O}$	10	0.0180	1.8
	20	0.0150	2.6
	30	0.0129	3.5
$\text{AIR}/\text{H}_2\text{O}$	10	0.0227	2.0
	20	0.0185	2.5
	30	0.0157	3.2

The diffusion coefficients were compared by the authors with earlier measurements and appear to be reliable within the estimated average experimental error of 10%.

Bubble Cloud. In the application contemplated, the bubble volume density required is expected to be small. Zwick<sup>23</sup> shows that the velocity of sound is reduced to  $8.3 \cdot 10^4$  cm/sec by a volume fraction of small bubbles of  $10^{-4}$ . The minimum sound velocity is near 20 m/sec for 50% by volume of tiny air bubbles. For a volume fraction of  $10^{-4}$ , Zwick's analysis indicates that there would be little flow interaction between bubbles, provided the largest did not leave a turbulent wake. The velocity of rise of bubbles of each size can therefore be taken the same as for an isolated bubble.

Summation: bubble dynamics. In the absence of a workable theoretical analysis, bubble life predictions must be based on an approximate analysis or on empirical data. Hammerton and Garner<sup>24</sup> give curves for hydrogen and oxygen mass transfer coefficients for bubbles in distilled water. In the range  $0.1 < r < 0.3$  cm, the ratio of the coefficients is about 1.5. For small bubbles (less than 0.15 cm radius) the transfer rate for ethylene bubbles decreases rapidly, approaching the Frossling equation for rigid spheres. No measurements were given for bubble radii less than 0.1 cm, where the results are most needed.

The experimental techniques reported in the literature indicate the difficulties of obtaining repeatable measurements and particularly of avoiding systematic effects. A study of small hydrogen bubbles in sea water is needed, but the task of getting meaningful data will be demanding.

If the interaction of the diffusion coefficients is neglected the problem solution can be analyzed in terms of partial pressures across the bubble wall, following London, Calderbank, and Coward.<sup>25</sup> The inclusion of the inward diffusion of oxygen and nitrogen and a more suitable rise velocity to replace the Allen relation used by them are needed.

The simple case analyzed by Turner<sup>8</sup> of air bubbles released at a depth of 1.37 meters in tap water saturated with air is instructive. He finds a critical radius (for the stated conditions) of 0.006 cm. Smaller bubbles dissolve after a limited rise whereas larger ones reach the surface. Blanchard and Woodcock,<sup>26</sup> extending the work of Wyman et al.,<sup>27</sup> give a graph of solution times for air bubbles in sea water at a depth of 10 cm as a function of bubble diameter and of percentage of air in the water. Curves for saturated sea water at depths of 1 cm and 100 cm are superposed.

The flow interaction of small bubbles in a cloud appears to have negligible effect on the rise velocity of the individual bubbles.

### III. Applications Principles

The prompt creation of a curtain of bubbles of the desired size distribution to a depth of, say, 15 meters requires that bubbles of all needed sizes (for resonance radii of the desired frequencies) be created throughout the volume to be treated.

The interaction of a sound wave with a bubble is strongest at resonance; the behavior off-resonance has not been determined, but the evidence points to a relatively high  $Q$  for the bubble, hence a rather rapid decrease in effect with frequency deviation from resonance. The resonance frequency given by Flynn<sup>28</sup> is

$$\omega_o^2 = \frac{1}{r_n^2 \rho} \left\{ b \left( p + \frac{2\sigma}{r_n} - p_v \right) - \frac{2\sigma}{r_n} \right\}$$

where

- $r_n$  = equilibrium radius,
- $\rho$  = liquid density,
- $p$  = liquid pressure,
- $\sigma$  = surface tension,
- $p_v$  = vapor pressure,
- $3 \leq b \leq 3\gamma$  ;  $\gamma$  = ratio of specific heats of the gas.

This equation is based on the incompressibility approximation; the liquid density is assumed constant and the velocity of sound infinite. The parameter  $b$  is equal to 3 for isothermal compression of the gas; for adiabatic compression,  $b = 3\gamma$  .

The usual approximation takes  $b = 3\gamma$ , neglects  $p_v$  and  $\sigma$ , whence



$$r \cong \frac{0.326}{f} \left( \frac{h + 10}{10} \right)^{\frac{1}{2}}$$

where  $r$  = radius in cm ( $20^{\circ}\text{C}$ ),

$f$  = frequency, kHz

$h$  = depth in meters.

Not only is a larger radius needed for resonance at a depth of 15 meters in the ratio 1.58 because of the increased stiffness of the bubble, but also a larger STP volume because of the hydrostatic pressure of 2.5 atmospheres. The required volume of gas at 15 meters depth is therefore nearly 4 times that needed at the surface.

By the time the desired distribution of bubble sizes to a given depth is achieved, deterioration is in progress. Since the change in radius due to diffusion appears to be in the vicinity of  $5 \cdot 10^{-5}$  cm/sec for air bubbles in saturated sea water<sup>27</sup> and about twice as much initially when hydrogen is present, small bubbles will shrink to ineffectiveness. Bubbles of radius 0.03 cm, corresponding to 11 kHz near the surface will rise at 7 cm/sec or 0.4 meter/min. Since the increase in radius with decreasing depth approximates the shrinkage, the prime effect at this size is the rise of the curtain. If the depth is unlimited, the curtain could be replenished by bubbles rising into the required region but only the larger bubbles will be supplied.

Bubble generation. The purpose of the experimental work was to demonstrate that bubbles corresponding to each size of particle of LiH could be produced. Lithium metal is available from Lithium of America in a nominal size distribution from 30 to 60 microns diameter, 30 wt% in an oil

suspension at a cost comparable to LiH. The relative ease of achieving a desired size distribution with powder, however, indicates that LiH is more promising. Furthermore LiH yields 12.6 gm moles  $H_2$ /gm vs. 7.2 for Li, or 9.8 gm moles/cc vs. 3.8 for Li.

The objective is to achieve an independent bubble for each particle of powder. Agglomeration must be avoided and each particle, when it begins to react on contact with water, must be attached to the surface of the bubble so that the complete yield of  $H_2$  is released in that bubble and not in a series of separate bubbles. Once formed, the bubble must resist fusion with neighboring bubbles so that the distribution is retained. An adequate supply of surfactant will assist in maintaining isolation. Even though sea water generally appears to be well-supplied with surfactant, addition of a known effective material to the mixture will assist in dispersion of the bubbles.

Experimental work was concentrated on the preparation and test of a liquid suspension of commercially available LiH powder. The carrier liquid must be readily soluble in water to provide immediate reaction and gas production. The first experiments were done with acetone (dimethyl ketone) density 0.792 (20°C) boiling point 56.5°C, infinitely soluble in water. The density closely approximates that of LiH, 0.78 (25°C) (Lithium Company of America). The purity of the powder available from Lithium Company and Foote Mineral Company is typically 96% pure: some LiOH is usually present. The hydroxide has a density of 1.46: a uniform 4% composition of LiOH would indicate a density of ~ 0.81. It was noted that the powder would settle in acetone. There was also a slow reaction of LiH with acetone with liberation of appreciable gas after 12 hours.

Methyl ethyl ketone, MEK, (2-butanone) (Fisher reagent) density 0.805 (20°C) was dried with LiH; thereafter liberation of gas was inappreciable. Since much of the LiH settled out of MEK, about 20% Union Carbide Tergitol NPX was added. A reaction indicated that the Tergitol had taken up water, since it is hygroscopic. The increased viscosity assisted in keeping the LiH suspended. On injection of the mixture in a tank from a hypodermic syringe, bubbles of 0.01 cm diameter (by inspection) and smaller were formed. At this high percentage of NPX, however, a slow ejection from a 10 milli-inch hypodermic needle resulted in strings of suspension which reacted slowly with the water.

Tergitol XC, a waxy solid, was then tried in MEK; 1% LiH and 1% XC. Overnight a substantial portion of powder had floated to the surface, a smaller portion settled out, but a dense milky central portion indicated a considerable retention in suspension.

The possibility of a reaction with the ketones led to the substitution of tetrahydrofuran, THF, (1,4-epoxy butane) as the liquid carrier. The density of THF, 0.89 (21°C), F.P. -65°C, B.P. 64-5°C, is 15% higher than the nominal density of LiH. With a 0.01 gm/cc slurry of LiH, however, a three-part separation again occurred. Analysis of the suspended slurry from mid-column indicated a concentration of 1.5 mg/ml, i.e., that 15% of the total solid was suspended.

A mixture of 60 gm of LiH powder in 350 ml THF was made up and thoroughly mixed. The slurry was then centrifuged at 3400 g's for an hour, the three layers separated, the solids recovered, and each component analyzed with the Micromerograph. The particle size distribution of the suspended portion was close to that of the original powder, given below. The powder recovered from the bottom sediment was about 1 $\mu$  smaller at each weight per-

cent. The floating layer, however, consisted of larger particles. The powder used in this experiment was Foote Mineral Company nominal  $8\mu$  LiH. The dry powder Micromerograph analysis is compared with the separated components in the following table. The equivalent spherical diameter is given as a function of weight percent less than that indicated.

Weight Portion less than	Equivalent Spherical Diameter			
	Original	Suspended	Bottom	Top
10%	3.8 $\mu$	4.3 $\mu$	3.8 $\mu$	6.5 $\mu$
20	5.0	5.8	4.9	8.7
30	6.3	7.1	5.9	11.0
40	7.6	8.1	6.7	13.0
50	8.9	8.9	7.8	16.0
60	10.6	9.9	9.1	18.0
70	12.4	11.4	11.0	21.0
80	15.0	15.0	13.0	25.0
90	19.0	20.0	17.0	33.0

A shipment of Lithium Co. lithium metal in mineral oil was now available so it was included in the experiments. The specifications given by the Company are 1% sodium in the metal. The dispersion used was 30% metal, 69% mineral oil and 1% oleic acid. Under the microscope, the metal particles approach a spherical shape, of size range from  $3\mu$  to  $55\mu$ , median about  $15\mu$ . The resulting gas bubbles should range from about  $30\mu$  to  $500\mu$  NTP, substantially larger than the range from LiH powder.

Coulter Counter. Much effort was expended to calibrate the Coulter Counter over the desired particle size range. Great difficulty was experi-

enced in keeping 100 $\mu$  pollen grains in suspension in the circulating system of 2 liters capacity devised for the measurement of bubbles in the expected size range.

Added difficulty was experienced, as noted above, in obtaining a liquid suspension which could be injected for the conversion of particles to bubbles. A 2cc syringe propelled by a motor-driven screw delivered 0.1 ml of slurry/min or 0.035 ml in the 20.7 second counting period. The slurry was delivered through a No. 26 hypodermic needle (ID 0.01 inch) into a restriction in the glass channel where the velocity was 20 cm/sec, thence into a broader channel at a velocity of 2 cm/sec. The counting orifice was located 20 cm above, at 10 seconds delay from the injection point.

A reasonably repeatable counting system was achieved when two 0.1 inch stainless balls were placed in the syringe chamber and agitated by an adjacent magnetic stirring drive. The preliminary measurements indicated that the bubble size distribution followed in a general way that computed from the Micromerograph data. The low total gas volume showed the serious loss of particles in the preparation procedure and particularly in obtaining a representative delivery of slurry from the syringe. By the time these difficulties were under control, time was running out. Attention was turned, therefore, to solid mixes, since this approach held more promise of practicable system.

Solid Mixtures. Pellets were made of lead powder and both LiH powder and Li in oil. When these pellets were dropped in a small tank, the gas bubbles in formation were attached to the pellet and provided considerable buoyancy. Pieces 1/8 inch across would not sink at all. Pellets of 1/4 inch diameter and larger would fall rapidly enough to keep the forming bubbles swept away.

The following compositions were made up:

Li-1	14.15%	Lithium Metal 30% in oil
	85.1%	Lead Powder, Glidden Co. Grade F
	0.75%	Tergitol NPX Dispersant
Li-2	15.4%	Lithium Metal 30% in oil
	77.0%	Lead Powder, Glidden Co. Grade F
	7.6%	Tergitol XC Dispersant
LiH-1	10%	Lithium Hydride Powder
	80%	Lead Powder, Glidden Co. Grade F
	10%	Tergitol XC Dispersant

These mixtures were pressed into spherical or flat disk form for test.

A clear plastic tube 6 inches OD with 3/16 wall 6 feet tall was made into a tank so that a longer range of fall could be observed. A Mitchell 16 mm camera, operating at 128 frames/sec was set up to photograph the tube about 2- $\frac{1}{2}$  feet below the water surface.

The series of moving pictures indicated below were made. Except for serial C-1, lighting was from the back, two photofloods illuminating a white background. The run C-1 was made with one lamp at the side against a dark background. The improvement was apparent, even to the skeptical photographers.

Serial No.	Lens	Dist.	Pellet Formula	Tergitol Surfactant	Lighting
A-1 & 2 3 & 4	25 mm	5 ft.	Li-1 Li-2 LiH-1	NPX XC XC	Back
B-1 2 3	50 mm	4 ft.	Li-1 Li-2 LiH-1	NPX XC XC	
C-1	50 mm	4 ft.	Li-1	NPX	Side
D-1 2 3	100 mm	4 ft.	Li-1 Li-2 LiH-1	NPX XC XC	Back

A copy of the assembled and titled film was supplied to the sponsor. The velocity of fall of the pellet was estimated (from a frame count) at 50 to 65 cm/sec, about  $1/3$  the expected velocity of fall, indicating the buoyancy of the bubbles.

Even though the Li metal gave a much more copious supply of bubbles, more conspicuous in part because of the larger bubbles formed, the interpretation is that the reaction proceeds so fast that it will be difficult to control bubble production of the desired size. The liquid Tergitol, NPX, also goes into solution too rapidly. Even though the LiH powder produces a much less spectacular display, this combination appears more promising for the desired control of bubble population throughout extended volume. The bubbles spread laterally to fill the column within a few seconds. This spread is probably approaching the limit to be expected from a single falling source in a static liquid.

After the pellet reached the bottom of the tank, large bubbles accumulate on the generator and then rise. This effect is superfluous to the extended generation.

### Conclusions: Applications Principles

The experience gained in working with Li and LiH in a liquid suspension indicates that tetrahydrofuran is a suitable vehicle when vigorous stirring can be maintained. With addition of a surfactant such as Tergitol, separate bubbles are produced with a high likelihood of a bubble size distribution closely approximating the particle size distribution. With equipment meeting these requirements, a system for bubble curtain creation adjacent to a ship appears feasible. The problems of maintaining a uniform distribution in the slurry seems to limit the liquid carrier to this application.

A dispersion of Li or LiH in a compacted dense solid powder shows applicability to creation of a bubble curtain at a remote location. The active material could be compressed around a dense core so that the body would have the desired sinking rate. The active material pressed on the surface would be proportioned to the depth of bubble formation desired. For shallow depth, the inert core could be dispensed with in favor of simplicity. Protection against premature activation of the material could be provided by a cover removed at impact or by a dispenser which would burst before impact, scattering the generators over the desired area. An alternative would be individual round which could be fired from a machine gun with a cover removed on impact.



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